Replacement of Petroleum-based Rubber with "Bio-rubber" from Vegetable Oils

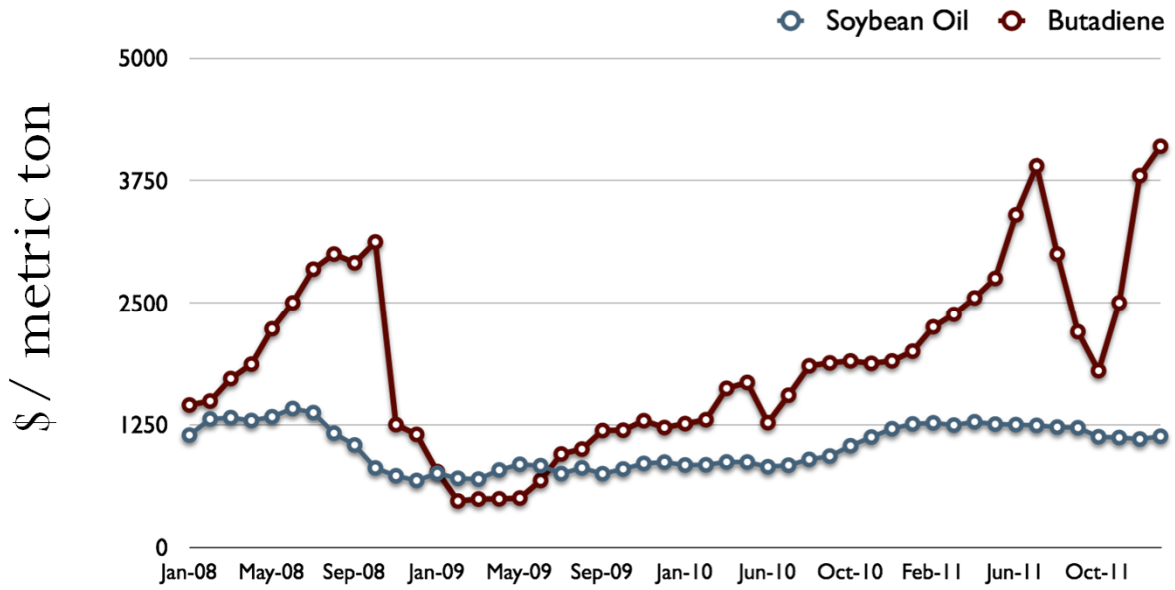
By: Chris Isely

Mentor: Dr. Eric Cochran

Chemical and Biological Engineering

Background

- The rubber industry has been dominated by petroleum based synthetic rubbers, especially those made from styrene-butadiene rubber (SBR).
- As awareness of the environmental effects and costs of petroleum have increased so has the need to find sutiable replacements.



Biopolymer

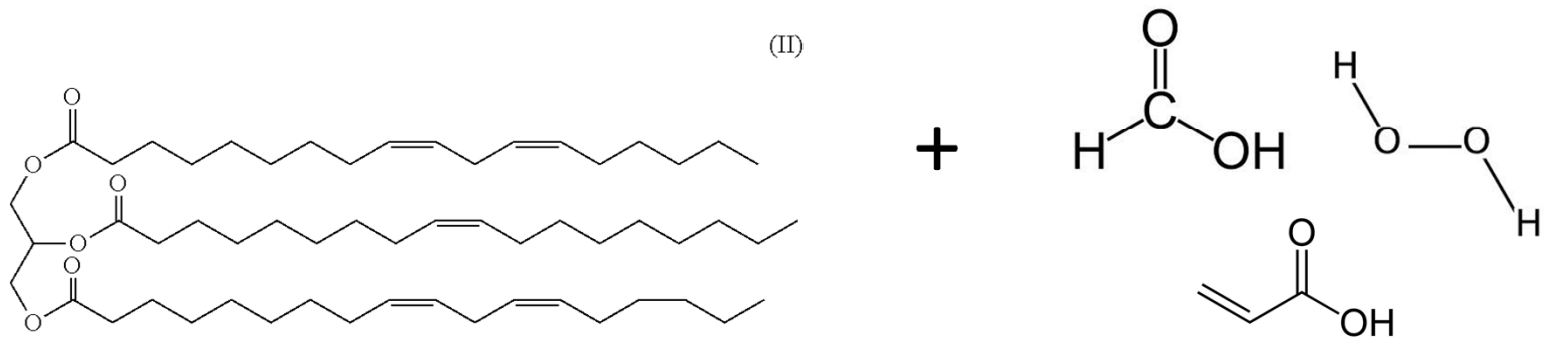
- A biopolymer
  - a polymer that is derived from a natural source, and is renewable.
  - Our research set out to find a suitable replacement to petroleum based products.
- Soybean Oil
  - We found that block copolymers of styrene-soybean oil produced similar properties as those of SBR type rubbers.

Method

- Soybean Oil
  - Triglyceride
  - About 4.6 double bonds
- Modification
  - Soybean oil was modified in order to improve reactivity and polymerization
  - Epoxidation and Acrylation
- Polymerization
  - Two methods used: ATRP and RAFT

Epoxidation and Acrylation

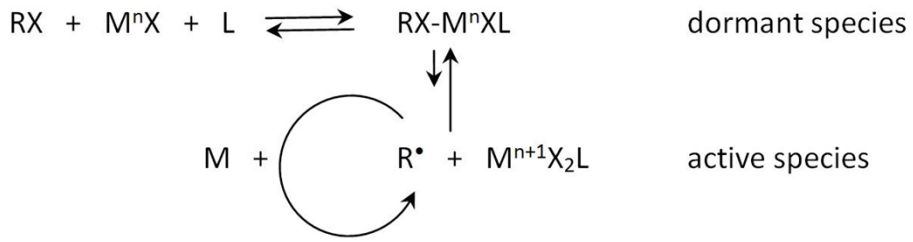
- Epoxidation performed through addition of formic acid, hydrogen peroxide.
- Acrylation performed through addition of acrylic acid



→ Acrylated epoxidized Soybean Oil (AESO)

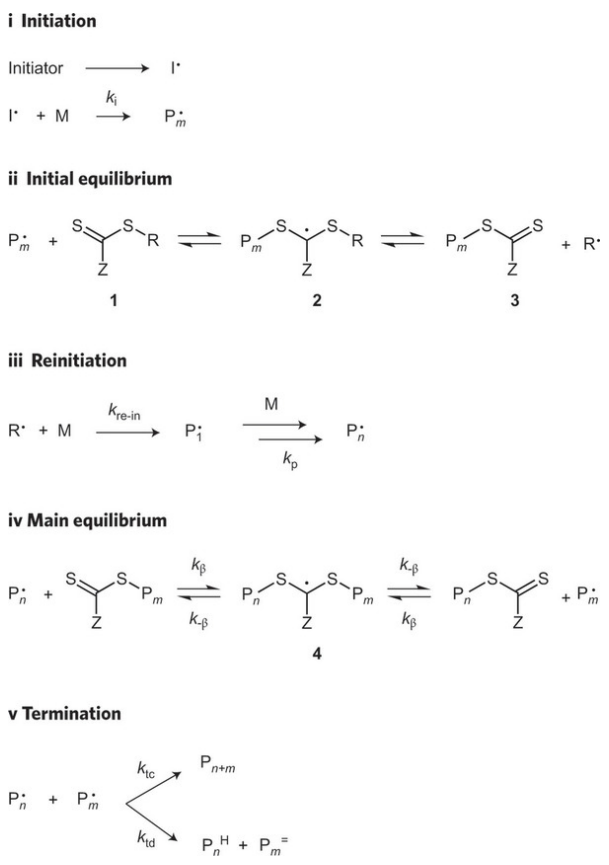
ATRP

- Atom Transfer Radical Polymerization
  - Controlled polymerization
- Reagents required
  - benzyl chloride as initiator
  - Copper 1 chloride as catalyst
  - Copper 2 chloride as counter catalyst
  - N,N,N',N,N Pentamethyl-diethylenetriamine (PMDETA) as ligand
- Varied temperatures of reaction, initiator concentration, solvent ratios, catalysts, and monomer concentration.



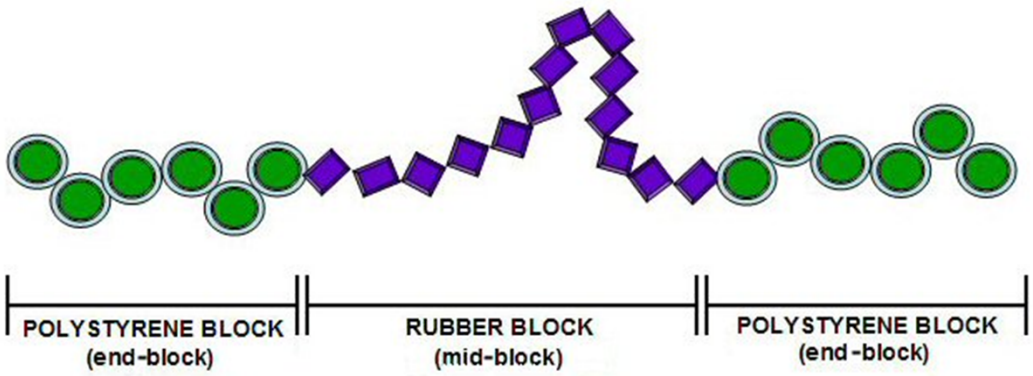
RAFT

- Reversible addition-fragmentation chain-transfer polymerization
  - Controlled polymerization
- Reagents used
  - AESO monomer
  - AIBN as initiator
  - Solvent
  - RAFT Chain Transfer Agent
    - Varied



Triblock copolymer

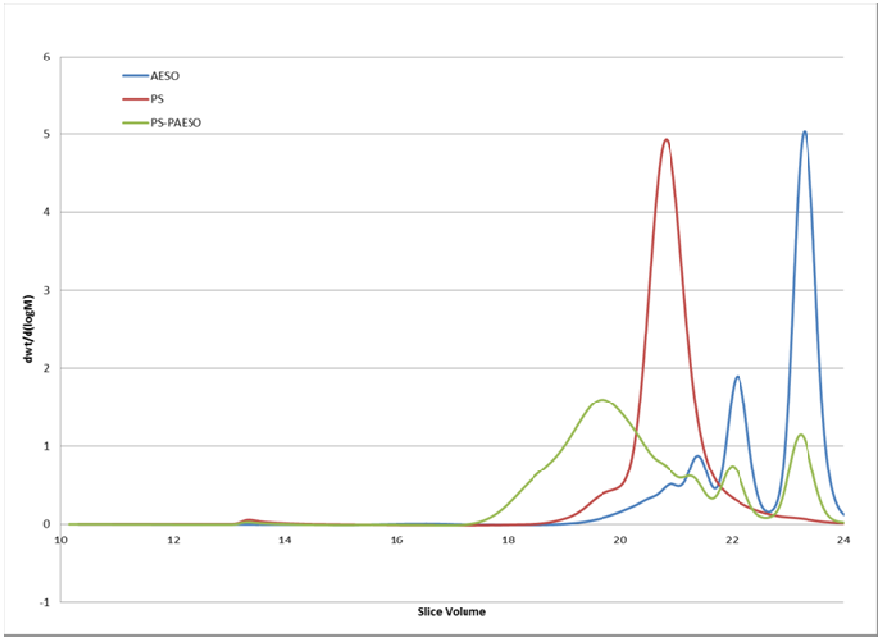
- Both ATRP and RAFT were used to make triblock copolomers from styrene and AESO monomers
- These polymers were SAS style in that they were Styrene-AESO-Styrene



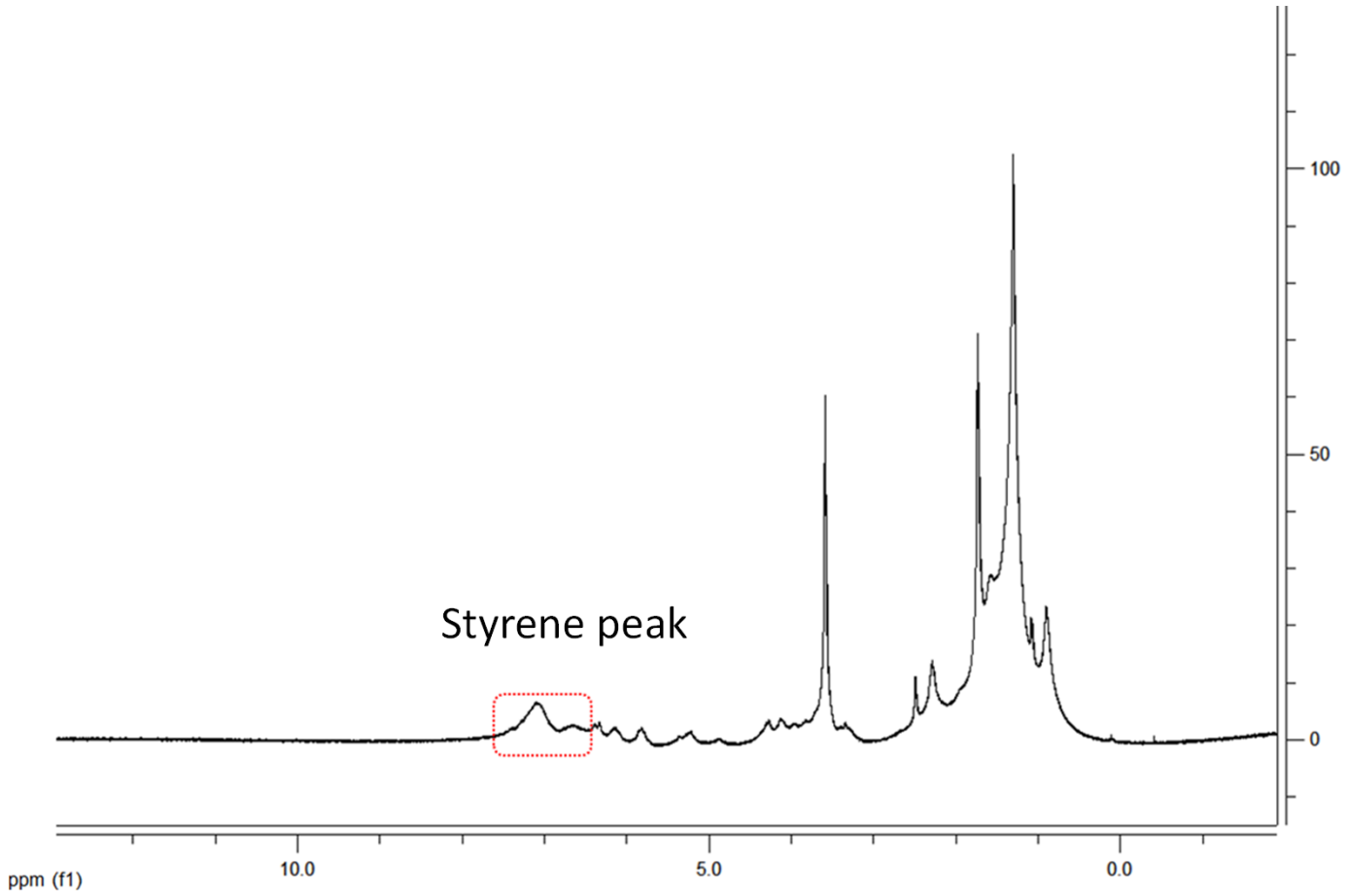
Products

- Varied:
  - Temperature, monomer/initiator concentration, solvent ratio, catalysts
  - Found rubbery viscoelastic properties
- We characterized our products using:
  - GPC, NMR, DSC, TEM

- GPC

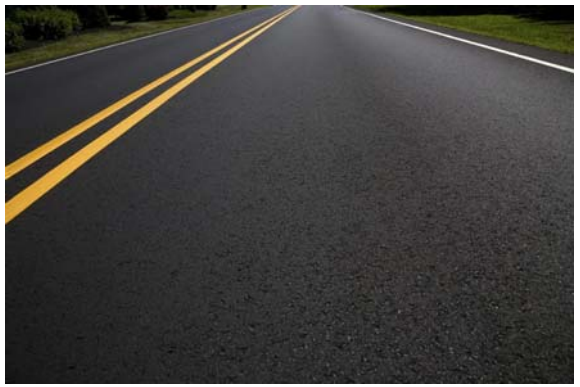


HNMR



Results

- Molecular weight
  - Molecular weights ranged from 10kDa to 1MDa
- Polydispersity
  - Measures range of Mw within a sample of polymer
  - PDI's were generally low, <2.0
- Viscoelastic properties
  - Similar to SBR type rubber
  - Properties suggest success in use as asphalt



Future Work

- Our results showed the effectiveness of controlled polymerization on a multifunctional monomer into a thermoplastic elastomer.
- Also showed promise as use as a rubber, and especially for use as an asphalt modifier.
- Our next goal will be scaling up of synthesis of this polymer, and involving companies in our work.

Works Cited

- http://www.oil-press-machine.com/Solution/oil_plants_solutions/soybean-oil-press.html
- http://en.wikipedia.org/wiki/File:Iowa_State_Cyclones_logo.svg
- Nacu Hernandez: ACS Presentation
- http://powerlisting.wikia.com/wiki/Rubber_Manipulation
- http://www.commodityonline.com/news/ncdex-soybean-bearish-until-closing-above-rs3230-52203-3-52204.html
- http://www.nature.com/nchem/journal/v2/n10/full/nchem.853.html
- http://www.eastman.com/Markets/Tackifier_Center/Pages/Block_Copolymer.aspx
- http://www.biobusinessaccelerator.com/pilot-plant/